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## Technical Report

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## Description of Progress

Studies of soluble and processable poly(3-alkylthiophenes) are continuing. Fibers of poly(3-decylthiophene) which were melt-spun at Celanese have been solution doped with  $\text{FeCl}_3$  and conductivities of  $5 \text{ S cm}^{-1}$  have been obtained. EDAX mapping of the dopant atom (Fe and Cl) distributions across the cross section of the fibers indicate homogeneous doping even using rather short doping times.

Polypyrrole/Poly(styrene sulfonate) molecular composites have been electrochemically prepared on stainless steel anodes. The polyelectrolyte carrier polymer imparts mechanical integrity to the films while also smoothing the morphology of the material compared to poly(pyrrole tosylate). Conductivities of  $40 \text{ S cm}^{-1}$  have been obtained for these materials.

Cyclic voltammetry in conjunction with scanning electron microscopy has proven to be useful as a fingerprint tool for the ion composition of polypyrrole membranes. These membranes were synthesized from a mixed aqueous/nonaqueous electrolyte medium containing naphthalene sulfonate as the dopant anion. The polypyrrole naphthalene sulfonate was then voltammetrically cycled in solutions containing  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and tosylate as the exchanging species. The cation ( $\text{Li}^+$  vs  $\text{t-Bu}_4\text{N}^+$  for example) was found to have a profound effect on the facility of this ion exchange process. Novel "memory" effects were also seen when the membranes were switched from one medium to another and then back; i.e. the voltammetric fingerprint was regained.

A new computational approach to estimating energy differences between the aromatic and quinoid forms of polyheterocycles has been developed. This method employs ab-initio molecular orbital theory on oligomers, with highly accurate extrapolations to the infinite system. A large number of polymers have been investigated, including polythiophene, poly(thieno[3,4-b]pyrazine), and poly(thieno[3,5-b]quinoxaline).

We have optimized the reactions conditions in the recently discovered 'bimechanistic' phase transfer catalyzed polythioetherification using sodium sulfide. Variables such as monomer concentration, catalyst concentration and structure have been studied. A critical finding of these studies is that bulk reaction conditions are not necessary for obtaining high  $M_n$  polymers of narrow

polydispersity. The best catalysts for the 'bimechanistic' system are dimethyl sulfide and pentamethylene sulfide. We are continuing to study some of the mechanistic factors involved in this reaction and extending our findings to the polymerizations of liquid crystalline (LC) polymers with extended conjugation.

New salen monomers have been prepared which contain terminal alkyl units as well as terminal unsaturation, i.e. methyl acrylates and acrylates. These LC monomers are being polymerized in order to prepare side-chain LC polymers.

## Publications

### Papers Published

Pomerantz, M., Cardona, R. and Rooney, P. "Application of the Perturbation Molecular Orbital Method to Aromatic Oligomers and Conducting Polymers", *Macromolecules*, **1989**, 22, 304.

Shaffer, T. D. "Phase Transfer Catalyzed Polymerization of  $\alpha,\alpha'$ -dibromoxylene Isomers", *J. Polym. Sci., Polym. Lett.*, **1989**, 27, 33.

Faulmann, C., Cassoux, P., Vicente, R., Ribas, J., Jolly, C. A. and Reynolds, J. R. "Conductive Amorphous Metal-Tetrathiolate Polymers: Synthesis of a New Precursor  $C_6O_2S_8$  and its Derived Polymers, and LAXS Structural Studies", *Synth. Met.*, **1989**, 29, 557.

Baker, C. K. and Reynolds, J. R. "Use of the Quartz Microbalance in the Study of Polyheterocycle Electrosynthesis", *Synth. Met.*, **1989**, 28, 21.

Ruiz, J. P., Gieselman, M. B., Nayak, K., Marynick, D. S. and Reynolds, J. R. "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes", *Synth. Met.*, **1989**, 28, 481.

Reynolds, J. R., Ruiz, J. P., Wang, F., Jolly, C. A., Nayak, K. and Marynick, D. S. "Electroactive and Soluble Polyheterocycles and Transition Metal Complex Polymers", *Synth. Met.*, **1989**, 28, 621.

Pomerantz, M. and Victor, M. W. "Synthesis and Characterization of a Series of Alternating Copolymers Containing Organophosphazene- $\lambda^5$ -azenes Backbone Moieties", *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)*, **1989**, 30(Number 1), 187.

Reynolds, J. R., Baker, C. K. and Gieselman, M. B. "Preparation and Characterization of Polyheterocycle/Polyelectrolyte Molecular Composites", *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)*, **1989**, 30(Number 1), 151.

Panchalingam, V. and Reynolds, J. R. "Synthesis and Characterization of Poly(vinyl acetate-co-vinylidene fluoride)", *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)*, **1989**, 30(Number 1), 179.

Shaffer, T. D. "PTC Polyetherification Through Nitro Displacement", *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)*, **1989**, 30(Number 1), 263.

### ***Papers in Press***

Pomerantz, M. and Victor, M. W. "Synthesis and Characterization of a Series of Alternating Copolymers (Oligomers) Containing Organophospha- $\lambda^5$ -azene Backbone Moieties", *Macromolecules*, in press.

Reynolds, J. R., Hsu, S. G. and Arnott, H. J. "The Effect of Growth Morphology on the Electrochemical Response of Poly(3-methylthiophene)", *J. Polym. Sci., Phys. Ed.*, in press.

Shaffer, T. D., Kramer, M. C. "Cyclization vs. Polymerization in Phase Transfer Catalyzed Polythioetherification", *Makromol. Chem.*, in press.

Basak, S., Ho, Y.-H., Tsai, E. W. and Rajeshwar, K. "Luminescent Probes of Ion Transport in Polypyrrole: New Strategies for Luminescence Modulations and Assay of Ion Content in Conductive Polymers", *J. Chem. Soc., Chem. Commun.*, in press.

Ho, Y.-H., Basak, S., Tsai, E. W. and Rajeshwar, K. "Optical Probes of Ion Transport in Electrochemical Processes Based on In Situ Derivatization: Application to Polypyrrole and Polythiophene Membranes", *J. Chem. Soc., Chem. Commun.*, in press.

Panchalingam, V. and Reynolds, J. R. "New Vinylidene Fluoride Copolymers: Poly(vinyl acetate-co-vinylidene fluoride)", *J. Polym. Sci., Polym. Lett. Ed.*, in press.

Shaffer, T. D. and Sheth, K. A. "Mesomorphic Transition Metal  $N_2O_2$  Chelates", *Mol. Cryst. Liq. Cryst.*, in press.

Ruiz, J. P., Reynolds, J. R., Nayak, K. and Marynick, D. S. "Soluble Ethylmercapto Substituted Polythiophenes", *Macromolecules*, in press.

Jang, G.-W., Tsai, E. W., Abraham, P. and Rajeshwar, K. "Charge Storage and Transport in Thermal Ruthenium Oxide Thin Films", *J. Electroanal. Chem.*, in press.

Reynolds, J. R., Jolly, C. A., Krichene, S., Cassoux, P. and Faulmann, C. "Poly(metal tetrathiooxalates): A Structural and Charge Transport Study", *Synth. Met.*, in press.

### ***Papers Submitted for Publication***

Shaffer, T. D. and Kramer, M. C. "Bimechanistic Phase Transfer Catalyzed Polythioetherification", *Macromolecules*, submitted.

Tsai, E. W., Basak, S., Ruiz, J. P., Reynolds, J. R. and Rajeshwar, K. "Electrochemistry of Some  $\beta$ -Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior", *J. Electrochem. Soc.*, submitted.

Nayak, K. and Marynick, D. S. "The Interplay Between the Geometric and Electronic Structures of Polyisothianaphthene and Polyisnaphthothiophene", *Macromolecules*, submitted.

Martinez, J. R., Chien, J.C. W., Wnek, G. E. and Reynolds, J. R. "Nuclear Magnetic Resonance of Conductive Polymers", *Macromolecules*, submitted.

Shaffer, T. D. and Sheth, K. A. "Mesomorphic Polyazomethine Ethers Containing Dibenzo-18-crown-6 Units", *Makromol. Chem. Rapid Commun.*, submitted.

### Meetings Attended and Papers Presented

Reynolds, J. R. attended the Society for the Plastics Industry Composite Meeting in Dallas, TX on February 6-8, 1989 and gave a presentation on the UTA polymer program.

Reynolds, J. R. and Pomerantz, M. attended the DARPA-University Research Initiative Program Review in La Jolla, CA on March 14-16, 1989.

### Visits and Invited Talks

Reynolds, J. R. visited the Naval Weapons Center in China Lake, CA on February 24, 1989 to discuss collaboration and give a research presentation.

Reynolds, J. R. visited the U.S. Army Electronics Technology and Devices Laboratory in Fort Monmouth, NJ on March 28, 1989 to discuss collaboration and give a research presentation.

### Visitors to UTA

Contract monitors David Squire and JoAnn Milliken visited our site on January 19, 1989 to discuss the progress of our URI program.

Rockwell Science Center representatives Fred Raniere and Les Warren visited on January 20, 1989 and discussed collaboration.

Professor Lon Mathias of the University of Southern Mississippi visited and gave a lecture on February 7, 1989 entitled "Crystallinity and Conformation by  $^{15}\text{N}$  Solid State NMR of Nylons".

### Personnel Change

Dr. Ursula Wettermark of General Dynamics in Fort Worth has begun as a visiting scientist for one year.